

# CODING FORM FOR SRC INDEXING

Microfiche No.		
OTS0538139		
New Doc I.D.	Old Doc I.D.	
86-930000145		
Date Produced	Date Received	TSCA section
1/25/93	3/04/93	8D
Submitting Organization		
INTL ISOCYANATE INST		
Contractor		
Document Title		
RISK ASSESSMENT ANALYSIS FOR SOME KEY ISOCYANATES WITH COVER LETTER DATED 022393		
Chemical Category		
2, 4-TOLUENEDIISOCYANATE (584-84-9)		

8d

INTERNATIONAL ISOCYANATE INSTITUTE, INC.

"Contains NO CBI"

119 CHERRY HILL ROAD  
PARSIPPANY, NEW JERSEY 07054  
TELEPHONE (201) 263-7517  
FAX (201) 263-8739

93 MAR -4 AM 8:29

February 23, 1993

34 pages

86930000145

SENT BY CERTIFIED MAIL

TSCA Document Processing Center (TS-790)  
Office of Pollution Prevention & Toxics  
Environmental Protection Agency  
401 M Street, SW; 201 East Tower  
Washington, D.C. 20460



86930000145

Attn: 8(d) HEALTH & SAFETY STUDY REPORTING RULE (REPORTING)

Dear Sir or Madam:

As required by 40 CFR 716, as amended, we herewith submit a copy of the following recently completed health and safety study.

Risk assessment analysis for key isocyanates. Project AM-E-92.

<u>Chemical Name</u>	<u>CAS Number</u>
2,4-Toluenediisocyanate	584-84-9
2,6-Toluenediisocyanate	91-08-7
4,4'-Diphenyl methane diisocyanate	101-68-8

The International Isocyanate Institute (III) project identification number, **AM-E-92**, has been marked as part of the title of this report. Please refer to this III identification number in any communication regarding this study. **The enclosed report does not contain any Confidential Business Information.**

This study is sponsored by the International Isocyanate Institute on behalf of the following:

The Dow Chemical Company  
Miles, Inc.  
BASF Corporation  
ICI Americas, Inc.  
Olin Corporation

Very truly yours,

R. K. Rigger  
Managing Director

RKR/sha

# ***REPORT***

*Title*

RISK ASSESSMENT ANALYSIS FOR SOME KEY  
ISOCYANATES

*Author(s)*

W. BROCK NEELEY

*Contractor*

EnvironSoft Inc.  
P O Box 2566,  
Midland, MI48641, USA

*Observations*

The Institute has current projects to determine more  
precisely data used in this risk assessment.  
Accordingly, the Scientific Office should be contacted  
for the current state of knowledge, and more recent risk  
assessments.

*III Project*

AM-E-92

*III File Number*

10890

93.01.25

*Date of III issue*



INTERNATIONAL ISOCYANATE INSTITUTE INC.

Head Office; 119 Cherry Hill Road, Parsippany, New Jersey 07054, USA.  
Scientific Office; c/o P.O. Box 42, Hexagon House,  
Blackley, Manchester M9 3DA, England.

Title page to all members. Full Report to:

<b>R F Hoffmann</b>	ICI	<b>M Mann</b>	BAYER	<b>N Tohms</b>	TAKEDA
<b>M Blankenship</b>	DOW	<b>P Davies</b>	ICI	<b>T Sose</b>	SBU
<b>L L Jackson</b>	DOW	<b>C Bastian</b>	DOW	<b>H Kitahara</b>	NPU
<b>R Bailey</b>	DOW	<b>M Bourguignon</b>	ECI	<b>S Michishima</b>	DMK
<b>M T French</b>	OLIN	<b>J M Dobbs</b>	ZENECA/ICI	<b>H Tachibana</b>	MITSUI
<b>C Grigsby</b>	BASF	<b>J Hutchison</b>	BASF		
<b>F Menezes</b>	PRONOR	<b>W Klebert</b>	BAYER		
<b>R Notaro</b>	ICI	<b>J C Parron</b>	RHÔNE-POULENC		
<b>R Ode</b>	MILES	<b>B Reeve</b>	SHELL		
<b>P Rubbe</b>	BASF	<b>K S Brenner</b>	BASF		
<b>J H Chapman</b>	MILES				

Summary

"See Appended (pp27-8)"

AM-E-92

10890

## RISK ASSESSMENT ANALYSIS FOR SOME KEY ISOCYANATES

by  
W. Brock Neely  
EnviroSoft, Inc.,  
P.O.Box 2566, Midland, MI 48641

Production figures (Frey et al. 1990) indicate that 741 million pounds of the 80:20 mixture of 2,4- and 2,6- Toluene Diisocyanates (2,4-TDI and 2,6- TDI) were manufactured in the United States in 1988. At the same time the production in Western Europe and Japan had reached 759 and 211 million pounds respectively for a total of 1.7 billion pounds. The figures for the 4,4' Diphenylmethane Diisocyanate (4,4'-MDI) were equally dramatic for the United States, Europe and Japan being 934, 1012 and 321 million pounds for a total of 2.3 billion pounds. These numbers are expected to expand since the demand for foams, elastomers and coatings continues to increase. When the magnitude and growth rate for these monomers are compared to other big volume products (C&EN,1991) than it becomes apparent why the government has expressed concern about the potential for health and environmental risk from these chemicals. The monomers to be discussed in this report are shown in Figure 1.

### RISK ASSESSMENT

In order to have a common basis for understanding it will be well to define what is meant by risk assessment. This is a phrase that has been used and abused for many years. The controversy and conflict surrounding its use caused the government to enlist the services of the National Academy of Sciences to address the issue.

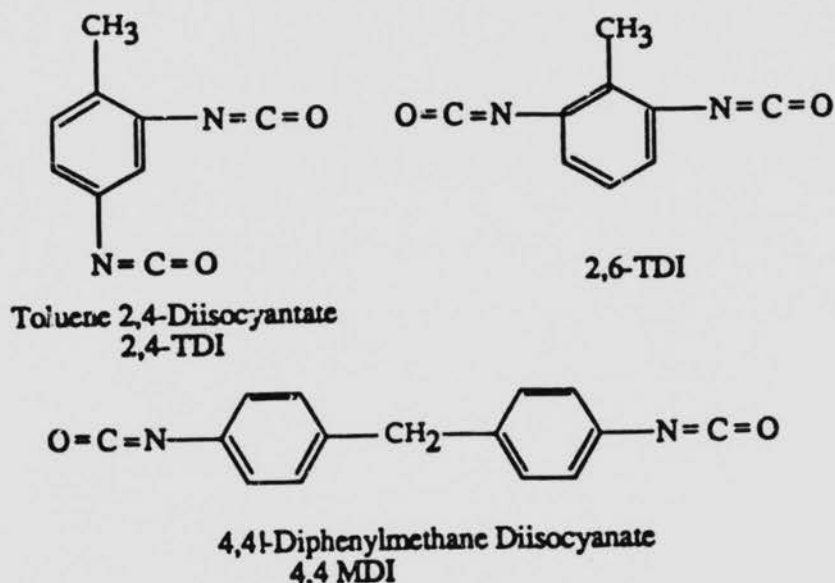


Figure 1. Structure of the Diisocyanate monomers to be discussed in this report.

One of the conclusions was that risk assessment is a prelude or input to the overall risk management operation and the distinction between the two processes ( i.e. of assessment and management ) should be sharply defined. The former is the use of a factual scientific base to define and interpret health effects of exposure of individuals and populations to hazardous materials and situations. The management side of the process involves choices between the broader social and economic values. This paper will not discuss the management question but will concentrate on the assessment question. In this connection the Academy outlined the following items that need to be considered in performing a risk



assessment (NAS, 1983).

1. Hazard Identification
2. Dose-Response Assessment
3. Exposure Assessment
4. Risk Characterization

The Environmental Protection Agency (EPA, 1986)) issued guidelines for performing a risk assessment and the above four elements were an integral part of the procedure.

The remainder of this report will follow these guidelines in assessing the potential risk from the isocyanate monomers shown in Figure 1.

## 1. Hazard Identification

This is a process of determining whether exposure to an agent can cause an increase in the incidence of a health condition (cancer, birth defects, etc.) and or any environmental impact other than health. The elements involved in making a hazard identification are the following:

- ...Physical and Chemical Properties
- ...Toxicological Effects
- ...Route of Exposure

a. Physical and Chemical Properties - The chemical and physical properties of the isocyanates have been summarized (Bailey, 1991) and are shown in Table I. The properties for the 2,4-TDI are those reported in the Handbook for Environmental Data (Verschuere, 1983). A draft report (Chemical Biotesting Center, 1991) suggested a water solubility of less than 1 mg/L and the logarithm of the octanol water partition coefficient of 3.4 and 4.5 for TDI and MDI respectively.

The isocyanates in comparison with some other common chemicals such as ethylene glycol, benzene and 1,2-dichlorobenzene are not very volatile as may be seen from the data in Table 1.

The isocyanate ( $-N=C=O$ ) group is very reactive especially with nucleophilic reactants containing an acidic H atom. Thus carbamic



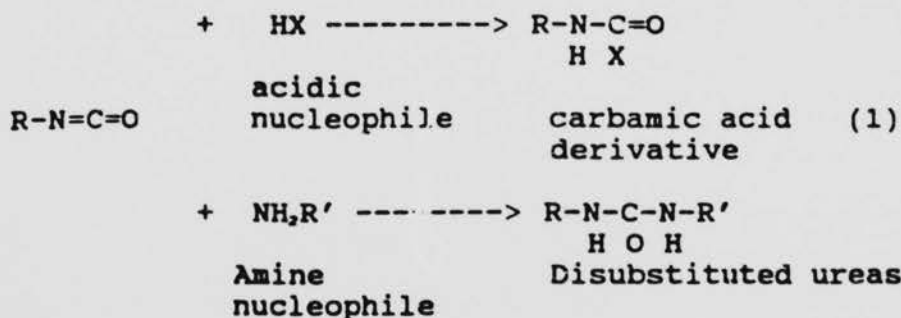
acid and urea derivatives are formed as equation 1 indicates.

TABLE I

Properties of the three isocyanates compared to other chemicals

Chemical	Mol Wt.	Melt Pt. C	Boil Pt. C	Sp. Gr.	Vap. Press. Pascals <sup>1</sup>
2,6 TDI	174	18.2	246	1.22	2.6
2,4 -TDI	174	21	251	1.2	1.3
MDI	250	39	314	1.19	0.0014
Ethylene Glycol	62	-17	198	1.11	6.65
Benzene	78.1	5.5	80		10000
1,2-Dichloro Benzene 147		-16	179	1.3	133

<sup>1</sup> Measured at 20 - 25° Celsius



The order of reactivity of the various nucleophiles begins with the primary amines, followed by secondary amines, primary alcohols, secondary alcohols and water. Both water and secondary alcohols are the same reactivity and about 0.3 times as fast as primary alcohols (Bayer Chemical, 1991). Isocyanates are not very soluble in water hence the reaction occurs at the interface producing carbamic acid

which is unstable liberating carbon dioxide and forming a primary amine which in turn is very reactive toward the remaining isocyanate. The reaction as shown in equation 2 is second order in both water and the isocyanate.



The reactivity of the isocyanates with active hydrogen compounds at 100° C is shown in Table II (Bayer Chemical, 1991). On the other hand, the reactivity of a particular isocyanate toward a given alcohol, amine or any other active hydrogen (such as water) increases with increasing electrophilicity (electron attracting power) of the radical attached to the isocyanate group. The phenyl

=====

TABLE II  
Reactivity of the isocyanates at 100°C

Isocyanate <sup>1</sup>	Grouping Rate Constant x 10 <sup>4</sup> (L/mol.sec)		
	R-NH <sub>2</sub>	R-OH	Water <sup>2</sup>

2,4-TDI	36	21	5.8
2,6-TDI	6.9	7.4	4.2

<sup>1</sup> Aromatics are more reactive than aliphatic isocyanates

<sup>2</sup> Reaction with water has a high activation energy.

=====

group pulls electrons away from the isocyanate making it more positive and more susceptible to nucleophilic attack.

Morton and Deitz (Morton et al 1956) measured the reaction rate of phenyl isocyanate with water in dioxane at 80° C and found a second order rate constant of  $5.89 \times 10^{-4}$  liters/mole.sec. when the initial concentration of both reactants was 0.5 M. The constant k in equation 2 may be expressed by the following rate equation:

$$\frac{dx}{dt} = k (a-x) (b-x) \quad (3)$$

where a = [Phenyl isocyanate] initial concentration  
 b = [H<sub>2</sub>O] initial concentration  
 x = amount disappearing in time t

Integrating equation 3 yields equation 4.

$$k = \frac{1}{t(a-b)} \times \text{Ln} \frac{b(a-x)}{a(b-x)} \quad (4)$$

If b is in excess than the rate law follows a pseudo first order reaction as represented in equation 5.

$$k = \frac{1}{tb} \times \text{Ln} \frac{a}{(a-x)} \quad (5)$$

Thus in an aqueous solution the concentration of water is approximately 55 moles/liter. By multiplying the second order constant by 55 a pseudo first order rate constant of  $3.2 \times 10^{-2}$  sec<sup>-1</sup> is obtained. Since the reaction was run at 80° C the rate may be reduced by one half for every reduction of 10°C. Performing this calculation a rate constant for the hydrolysis of phenyl isocyanate at 20° C is  $5.1 \times 10^{-4}$  sec<sup>-1</sup> for a half life of about 25 minutes. The

relative rates of the TDI's and MDI are not expected to be much different. For purposes of this report  $5 \times 10^{-4} \text{ sec}^{-1}$  will be used for the psuedo first order rate constant for the hydrolysis of the three isocyanates. This is comparable to the 15-20 minute half life reported for TDI in water vapor (Grieverson et al, 1983) and is consistent with the rates observed in mixed heterogeneous systems (Kitano et al 1991).

Vapor phase hydrolysis of TDI has been studied at 27° C and with the relative humidity varying from 7-70%. Under these conditions no evidence was found for gas phase reactions between TDI and water (Holdren et al, 1984). The results indicate that removal of gaseous monomer from air is not dependant on water vapor concentrations, however, as the next section indicates the chemicals are subject to photo oxidation which serves as the primary means for destruction in the atmosphere.

The rate constant for photo oxidation in the atmosphere has been investigated (Becker et al, 1988) using a 420 L photo reactor at ambient pressure and temperature. The study generated a rate constant for TDI (80:20 mixture of the 2,4- and 2,6-TDI) of  $7.4 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$ . Assuming an atmospheric hydroxyl radical concentration of  $10^6 [\text{OH}] \text{ cm}^{-3}$  (Becker et al, 1988) the half life for TDI was estimated as approximately 26 hours.

b. Toxicological Properties - A summary of the toxicological data

for 2,4-TDI and MDI are reproduced in Table III (Kirk-Othner, 1981).

TABLE III  
Toxicological Data for the Isocyanates

Isocyanate	LD <sub>50</sub> rats g/kg	LC <sub>50</sub> rats in air mg/m <sup>3</sup> (h)	Subacute oral, rat daily dose deaths/ 10 d, g/kg no. fed
2,4-TDI	4.9 -6.7	350 (4)	1.5 3/6
MDI	11.6	370 (4) *	

It is assumed that the 2,6-TDI isomer has the same properties as the 2,4-TDI monomer.

\* This value has to be suspect since the vapor pressure of MDI will only support a saturated vapor concentration of 0.09 mg/m<sup>3</sup>.

Animal inhalation data (Verschuere, 1983) produced the following results. The LC<sub>50</sub> for rats exposed to the 2,4-TDI isomer for 4 hrs/day for 14 days was 14 ppm (98 mg/m<sup>3</sup>)<sup>1</sup>. Exposure of rats to 0.15 ppm of a mixture of 2,4- and 2,6- TDI in an inhalation chamber for 6 hrs/day, 5 days/week for 108 weeks did not effect tumor incidence (Loeser, 1983). Due to the reported irritating and sensitizing properties of the inhaled vapor (Kirk-Othner, 1981) the recommended maximum exposure for diisocyanates is 20 ppb (140 and 200 ug/m<sup>3</sup> for the TDI and MDI respectively) for a 10 minute period and a time weighted average exposure for a 10 hour day / 40 hour week of 5 ppb (35 and 50 ug/m<sup>3</sup>) (NIOSH, 1980 and Brochhagen et al, 1984).

<sup>1</sup> The conversion to mg/m<sup>3</sup> is as follows:  
mg/m<sup>3</sup> = (ppm x Mol Wt.)/24.5 at 25° C and 1 atmosphere.



Carcinogenicity via the oral route was conducted (NTP, 1980) using commercial grade of TDI and fed by gavage at a dose of 30 and 60 mg/kg for male rats and 60 and 120 mg/kg for females. The incidence of fibrosarcoma and cell adenomas were found to be dose related. As the next section will describe the oral route of exposure is not significant for the isocyanates. Thus the observation that these materials cause cancer when ingested is not a major concern when assessing the potential risk from exposure to either TDI or MDI.

Environmental toxicity has been performed on TDI and is summarized in Table IV.

=====

TABLE IV  
Environmental Toxicity for the various Isocyanates.

Species	Toxicity	Reference
Grass Shrimp (salt water)	508 mg/L <sup>1</sup>	Curtis, 1979
Fat head minnow (fresh water) <sup>2</sup>	164 mg/L ,96 hr LC <sub>50</sub>	Curtis, 1979
Red Wing Blackbird	100 mg/kg, oral LD <sub>50</sub>	Schafer, 1983

<sup>1</sup> Mortality was less than 65% at 96 hrs.

<sup>2</sup> An exposure of 164 mg/L for 24 hours caused 50% death.

=====

c. Route of Exposure - The normal route of exposure to isocyanates are through the skin or by inhalation. Of these the inhalation route is by far the most important. It has been estimated (Bayer Chemical, 1991) that TDI and MDI will yield a concentration in air of 255 mg/m<sup>3</sup> and 0.09 mg/m<sup>3</sup> respectively. The latter figure corresponds to the lower vapor pressure of MDI over TDI (Table II). The major industrial hygiene problem with TDI is the reported



sensitization of certain workers exposed to the vapors. The level of TDI in air detectable by odor is from 0.1 to 1 ppm (Kirk-Othner, 1981). This far exceeds the current Federal standards as reported previously (NIOSH, 1980).

## 2. Dose Response Assessment

This is the process of characterizing the relation between the dose of an agent and the incidence of an adverse health effect in exposed populations. It should take into account the intensity of exposure, age pattern of the population and other variables that might affect response, such as sex, lifestyle etc. A dose response assessment usually requires extrapolation from a high to a low dose and extrapolation from animals to humans. As can be seen this is a very complex subject and one in which data is frequently lacking.

Since the most important route of exposure is via inhalation the dose response relations for the isocyanates in air will be discussed. The best data that could be found is an extrapolation of work reported in the Handbook of Environmental Data (Verschuren, 1983) and reproduced in Table V. By assuming that the response is cumulative it is possible to state that 4 hrs/day for 14 days is equivalent to 56 hours of exposure and 6 hrs/day, 5 days/week for 4 weeks is equivalent to 120 hours. Thus a crude dose response curve for inhalation toxicity in rats can be created as shown in Figure 2.

=====

TABLE V  
Inhalation Toxicity for TDI in Rats

Time	Response (LC50) mg/m <sup>3</sup>
4 hour exposure	350
4 hrs/day for 14 days	98
6 hrs/day, 5 days/wk for 4 weeks	0.2 (no effect)

=====

While this data indicates a response relation it does not permit a quantification of a no effect level. The best that can be said is that for longer periods of

exposure time the dose required for the effect (i.e. 50% lethality) becomes smaller. At the smallest dose tested (0.2 mg/m<sup>3</sup>) there was no observable response to the equivalent of 120 hours exposure. Unfortunately, it is not possible to use Figure 2 to determine the no effect

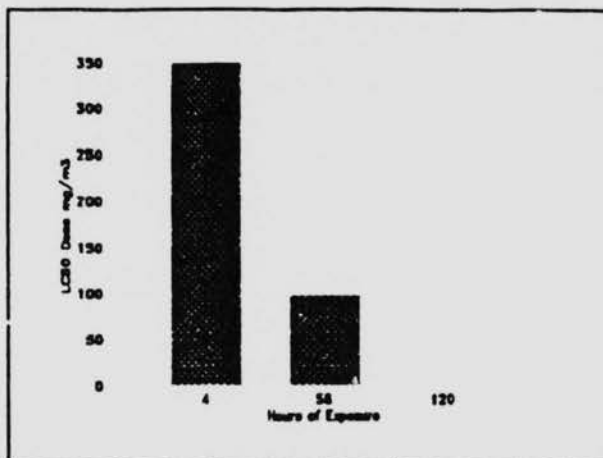


Figure 2 Dose Response Curve for vapor inhalation of TDI

response for an exposure lasting a life time. Until more definitive experiments are performed the government assessment for occupational exposure will be used as a starting point (NIOSH, 1980). Since the level of 5 ppb established by NIOSH is for a 10 hour day/ 40 hour week it will be divided by 10 and 0.5 ppb will be used as the maximum environmental exposure for the various isocyanates.

### 3. Exposure Assessment

From the previous discussion it was concluded that the maximum environmental exposure for the various isocyanates should not exceed 0.5 ppb. There are two scenarios that will be examined for comparing the exposure of these chemicals with the above criteria. The first is concerned with the exposure that might result to individuals in the vicinity of the manufacturing plants that are using isocyanates. The second deals with the importance of the concentrations that might be achieved in the environment from the long term world wide emission of isocyanates.

a. Scenario 1 (Site Specific) - TDI levels of 0.1 to 17.7 mg/m<sup>3</sup> (Grievesson et al, 1983) have been found in the stack gases from three German plants manufacturing flexible polyurethane foam. In order to model the downwind concentrations resulting from such a source it is necessary to know the diameter and the exit velocity of the stack gas. In the absence of such information reliance will be made on the data in Turner's Workbook (Turner, 1970). Assuming a stack diameter of 1 meter and a exit velocity of 10 m/sec. the volumetric flow rate from the stack will be 7.85 m<sup>3</sup>/sec. Using the maximum concentration of TDI found in the stack gas a source strength (Q in g/sec) for TDI may be calculated.

$$Q(\text{g/sec}) = 0.0177 \text{ g/m}^3 \times 7.85 \text{ m}^3/\text{sec} = 0.139 \text{ g/sec}$$

To estimate the concentration downwind from the stack, equation 6 (Turner, 1970) will be used.

$$C = \frac{Q}{\pi \sigma_y \sigma_z U} \exp\left[-\frac{1}{2} \left(\frac{H}{\sigma_z}\right)^2\right] \quad (6)$$

where C = concentration at ground level and in the center line of the plume.

$\sigma$  = is the standard deviation of the plume concentration distributed in the horizontal (y) and the vertical (z) direction.

H = the effective stack height.

U = wind velocity (m/s)

The standard deviations are a function of the climatic conditions and graphs and equations have been developed to take such items into account (Turner, 1970). The equations were solved using the computer package developed by EnviroSoft.<sup>1</sup> The results for two computer runs are shown in Table VI.

It will be noticed that as the stack height is increased to 100 m the concentration in the vicinity of the source is negligible (Figure 3). At 800 m the concentration reaches a maximum and then decreases. Only with a short stack height (20 m) and within 200 m of the source does the concentration of TDI exceed the limit of 0.5 ppb.

---

<sup>1</sup> A model based on dispersion analysis has been developed and packaged by EnviroSoft for solving these and other equations. For more information contact the Company at P. O. Box 2566, Midland, Mich. 48641.

TABLE VI

Concentrations of TDI downwind from two stacks with effective heights of 100 and 20 meters. The source strength was 0.14 g/sec with a wind speed of 4 m/sec during daylight hours with a temperature of 25° C.

Distance Km	Concentration (ppb) from a Stack Height	
	100 m	20 m
0.2	3.5 x 10 <sup>-5</sup>	1.3
0.4	0.0025	0.03
0.6	0.0069	0.02
0.8	0.0083	
1.0	0.0081	0.012
1.2	0.0074	
1.4	0.0070	0.007
1.6	0.0067	
1.8	0.006	
2.0	0.005	0.003

b Scenario 2 (Global Distribution) - What are the consequences of a gradually increasing input of isocyanates into the world over a period of many years? There have been many models designed to answer such questions (Baughman et al, 1978, Mackay 1979, Mackay et al 1985, Neely et al, 1982, Yoshida et al, 1987, Yoshida et al 1988). The basic model which has been called the Unit World is shown in Figure 4 where the major compartments are illustrated. The scaling is such that 510 million units are equivalent to the world (Neely, 1985). The volumes and physical properties for the model are shown in Table VII. In order to achieve a steady state situation for persistent chemicals such as DDT or the Chlorofluorocarbons there must be natural mechanisms for removing the material from the system. In the present model there are three



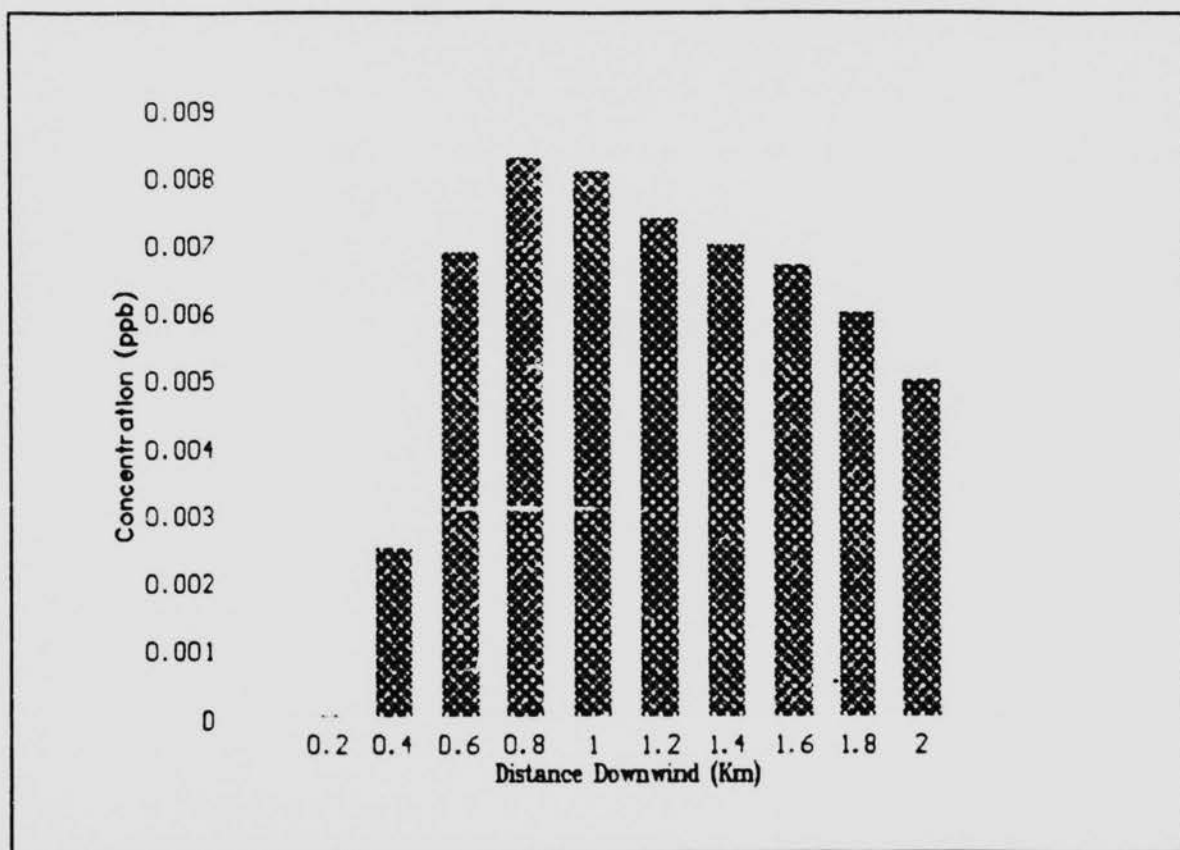


Figure 3 Downwind concentrations from a 100 m stack.

such mechanisms:

1. Exit to the stratosphere where the rate constant is based on the many mass balance studies that have been performed on the Chlorofluorocarbons (see for example Neely, 1977).

2. Removal from the active sediment layer on the bottom of the water column to the deep inactive layer of sediment.

3. Leaching through the ground beyond the 2 m depth (Neely *et al* 1986).

All chemicals added to the model are subjected to these three processes. Of the three the burial rate constant needs to be examined in more detail, the other two are adequately treated in the cited references.

Table VII

Environmental Parameters for the Unit World

Compartment	Volume $m^3$	Area $m^2$	Depth $m$
Air	$6 \times 10^9$		
Water *	$7 \times 10^6$	$7 \times 10^5$	10
Ground	$4.5 \times 10^4$	$3 \times 10^5$	0.15
Bottom Sediments	$2.1 \times 10^4$	$7 \times 10^5$	0.03
<u>Ground</u>			
Bulk density		$1.5 \times 10^6 \text{ g/m}^3$	
Water Content		0.2	
Porosity		0.4	
Fraction organic		0.02	
Air Content		0.2	
Slope		20 %	
<u>Bottom Sediments</u>			
Porosity		0.88	
Water Content		1.0	
Exit to Stratosphere		$4.1 \times 10^{-5} \text{ /day}$	
Burial Constant		$2 \times 10^{-4} \text{ /day}$	
Suspended sediments		5 ppm	
Average rainfall		0.7 m/yr	
Average temperature		25° C	

\* Water is 70% of the surface area of the world

In order to determine the burial rate constant it is necessary to investigate run off which in turn provides the sediment for the bottom layer. An analysis of field data (Neely et al, 1986) indicated that the rate constant  $k_b$ , (Figure 4) had values ranging from  $1 \times 10^{-4} \text{ /days}$  to  $7 \times 10^{-7} \text{ /days}$ . These covered a wide range

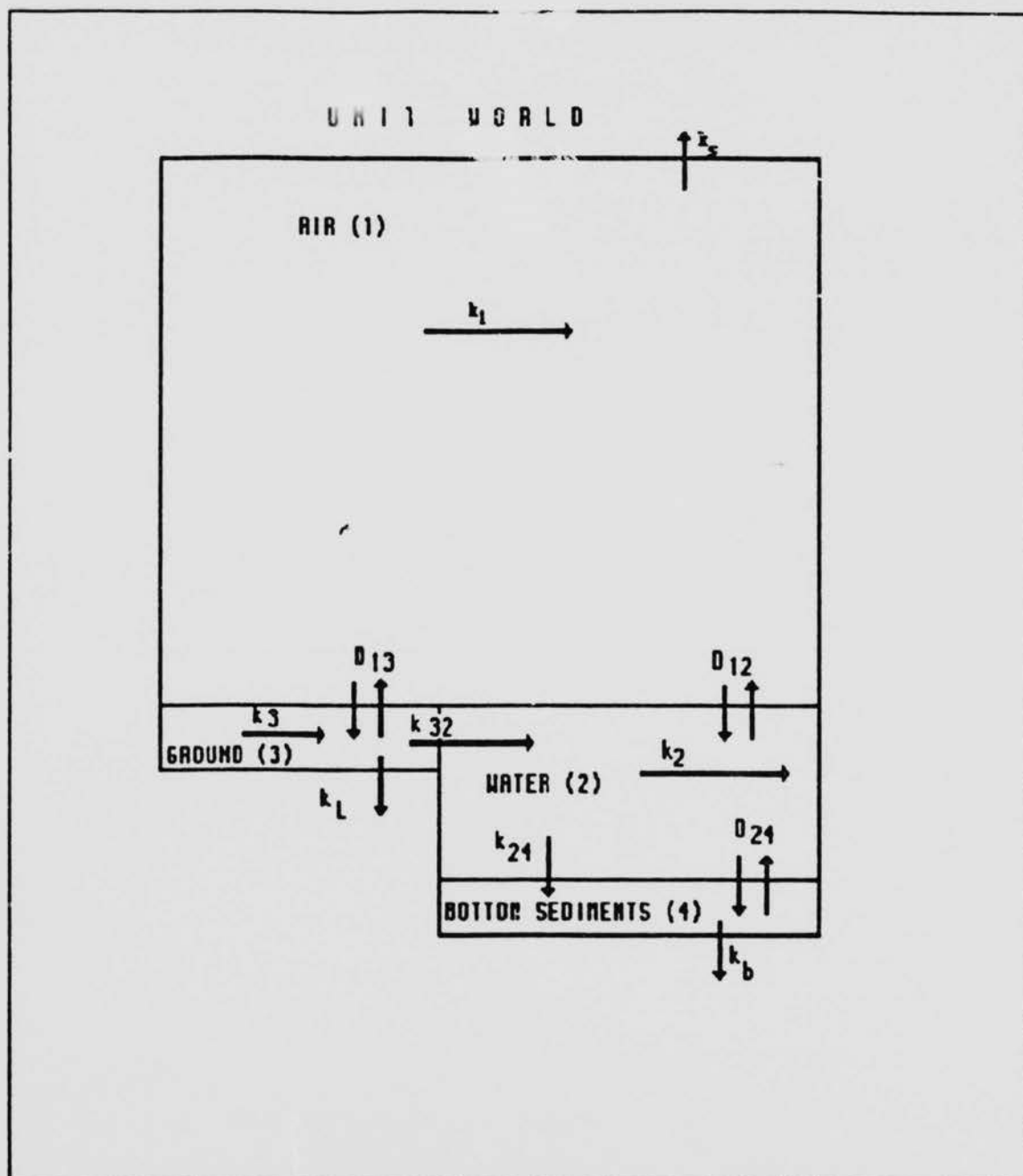


Figure 4 Schematic representation of the Unit World. The double headed arrows represent diffusion processes. The subscripts refer to the compartment numbers.

of soil types and slopes. For screening purposes a relationship between slope and  $k_{s2}$  was empirically established as shown in equation 7.

$$\log (k_{s2}) = 0.1 \times \text{Slope} - 7 \quad (7)$$

where  $k_{s2}$  is in reciprocal days  
and the slope ranges from 0 to 30 %

Thus for a slope of 20%  $k_{s2}$  has a value of  $10^{-5}$  /days roughly equivalent to the sediment loading for Lake Erie. Applying this value to the model shown in Figure 4 an average sediment yield is estimated by means of equation 8.

$$\begin{aligned} \text{Yield} &= (1 \times 10^{-5}) \times (0.15) \times (3 \times 10^5) \times (1.5 \times 10^6) \quad (8) \\ &= k_{s2}(\text{1/day}) \times \text{depth(m)} \times \text{Area(m}^2\text{)} \times \text{Density (g/m}^3\text{)} \\ &= 6.7 \times 10^5 \text{ g/day} \end{aligned}$$

Assuming a suspended sediment concentration of 5 mg/m<sup>3</sup> and a surface area of  $7 \times 10^5$  m<sup>2</sup> for the water compartment a sediment balance is performed as indicated in equation 9.

$$\begin{aligned} k_{s2} &= \text{Yield} / \text{Area} \times C_{ss} \quad (9) \\ \text{where } C_{ss} &= \text{concentration of suspended sediments} \\ k_{s2} &= \text{settling rate constant (m/day)} \\ &= 6.7 \times 10^5 / (7 \times 10^5 \times 5) \\ &= 0.19 \text{ m/day} \end{aligned}$$

From this analysis the burial rate constant may be estimated as follows. In one day ( $0.19 \times 5$ ) or 0.95 grams of sediment are deposited on 1 m<sup>2</sup>. Simultaneously, it will be assumed that an equal mass of soil became buried (i.e removed ~~from the active surface~~ of

the sediment layer). The burial rate constant is related to the first order process shown in equations 10-11.

$$\frac{dx}{dt} = k_b M_{soil} \quad (10)$$

where  $M_{soil}$  = the mass of soil in grams  
 $dx/dt$  = rate at which the soil is removed  
 = 0.95 g/day

Rearranging equation 10 yields equation 11.

$$k_b = (dx/dt) / M_{soil} \quad (11)$$

The total mass of sediment in the top 3 cm layer for an area of 1 square meter is given by equation 12.

$$M_{soil} = \phi (1 - \theta) \times \text{depth} \times 1 \text{ m}^2 \quad (12)$$

where  $\phi$  = bulk density  
 $\theta$  = porosity  
 =  $1.5 \times 10^6 \times 0.12 \times .03$   
 $M_{soil} = 5400 \text{ g}$

Thus the burial rate constant  $k_b$  is found from equation 11 using the respective values for  $dx/dt$  and  $M_{soil}$ .

$$\begin{aligned} k_b &= 0.95 / 5400 \\ &= 2 \times 10^{-4} \text{ /days} \end{aligned}$$

for a half life of 10.7 years.

The evaluation of the remaining rate constants and diffusion coefficients illustrated in Figure 4 have been described (Neely et al, 1986). The mass balance equations for each of the four compartments are derived in terms of fugacities (Mackay, 1979) and

solved by inverting the appropriate matrix.<sup>2</sup>

The one remaining difficulty in using the Unit World for estimating global concentrations is to define a suitable input. For the purposes of this model the world wide production of TDI and MDI will be used. The production of the former has been estimated at 1.7 billion pounds while MDI had a production of 2.3 billion pounds (Frey *et al.*, 1990). Since the size of the proposed model is such that 510 million units are equivalent to the world (Neely, 1985) the production figures will be scaled by this amount. Thus the input for TDI is 3.3 pounds/year and MDI is 4.5 pounds/year. This converts to 23 mmoles/day of TDI and 22 mmoles/day of MDI. Obviously, not all of this material escapes into the environment. Using a very conservative approach (Stephanson, 1979) assumed that a 0.1 of the production of benzene escaped. For this first analysis the same factor will be used. Accordingly the input of TDI and MDI will both be set at 2 mmoles/day into the Unit World.

In order to partially validate the Unit World as a technique for predicting environmental concentrations the insecticide DDT will be examined (Table VIII). Records indicate that world wide production of the chemical reached a level of 350 million pounds in the early 1970's (Neely, 1985). Dividing the value by 510 million and converting pounds to moles the equivalent input for the model

---

<sup>2</sup> The Unit World has been programmed by EnviroSoft and is presently being packaged for sale. For more information on this program contact the Company at P. O. Box 2566, Midland Mich. 48641.



becomes 2.4 mmoles/day. It will be further assumed that the entire production entered the environment - 75% to the ground and 25% to the water. The outcome is shown in Table VIII where several things should be noted.

1. The results are steady state values, in other words at steady state the output equals the input. The length of time required to reach this point is a measure of the persistence of the chemical. The longer the residence time the more persistent the material i.e. it takes longer to reach steady state. For DDT the residence time is 134 years. Since DDT is known to be persistent, 134 years becomes a benchmark to gauge persistence.

2. The numbers are not to be taken too literally, however, they do indicate a trend as to what might happen long term with the continued input of DDT.

3. By comparing the estimated water concentration of 42 ppt with the water quality criteria number of 1 ppt (Costle, 1980) it is apparent that exposure from DDT would become too great with continued long term heavy input of the insecticide.

4. In the case of DDT the final regulatory action was a ban on the use which resulted in a lowering of the input. This caused the exit rates to slowly begin the task of clearing the environmental compartments of the pesticide.

=====

TABLE VIII  
Results of adding DDT to the Unit World

Properties of DDT

Molecular Weight	354
Vapor Pressure	$2.6 \times 10^{-9}$ Pascals
Water Solubility	0.003 mg/L
Log Kow	6.00
Degradation constants were set equal to 0	
Input = 2.4 mmoles /day	
75% to the ground	
25% to the water	

Results

Residence Time	= 134 years
% in the water	= 0.72
% in the air	= 0.76
% in the ground	= 93.55
% in the bottom sediments	= 4.98
Concentration in water	= .042
Concentration in air	= .00005
Concentration in ground	= 864
Concentration in the Bottom sediments	= 98

=====

5. The results also indicate why there was so much effort applied to finding routes of degradation to supplement the three mechanisms of leaching, burial and exit to the stratosphere as a means of clearing the environment. If such a mechanism could have been found then the continued use of DDT might have been allowed.

The evaluation of TDI and MDI will be conducted in a similar manner to the above. The data in Table IX will be used for TDI while Table X contains the data for MDI. Examining the results in Table IX it can be seen that the final concentrations are very small and far below the 0.5 ppb level set for the maximum environmental exposure. Splitting the input 50:50 between air and water had very little

effect on the final result. The residence time was half as large and the concentration in water increased slightly to the  $10^{-7}$  ppb level. The results for MDI are shown in Table X and for the most part are comparable to TDI.

TABLE IX

Results of adding TDI to the Unit World

Properties of TDI

Molecular Weight	174
Vapor Pressure	2.6 Pascals
Water Solubility	100 mg/L
Log Kow	2.00

Degradation constants

Air rate constant	= .64 /day
Water hydrolysis	= 43 /day
Ground degradation	set equal to 0
Input	= 2 mmoles /day
	100% to the water

Results

Residence Time	= .004 years
% in the water	= 0.05
% in the air	= 99.94
% in the ground	= 0.00
% in the bottom sediments	= 0.00
Concentration in water	= $4 \times 10^{-8}$ ppb
Concentration in air	= $9 \times 10^{-8}$ ppb
Concentration in ground	= $1 \times 10^{-8}$ ppb
Concentration in the Bottom sediments	= $9 \times 10^{-8}$ ppb

=====

TABLE X

Results of adding MDI to the Unit World

Properties of MDI

Molecular Weight	250	
Vapor Pressure	0.00014	Pascals
Water Solubility	10	mg/L
Log Kow	1.5	

Degradation constants

Air rate constant = .64 /day  
Water hydrolysis = 43 /day  
Ground degradation set equal to 0  
Input = 2 mmoles /day  
100% to the water

Results

Residence Time	= .004 years
% in the water	= 0.06
% in the air	= 99.67
% in the ground	= 0.27
% in the bottom sediments	= 0.00
Concentration in water	= $7 \times 10^{-8}$ ppb
Concentration in air	= $1 \times 10^{-7}$ ppb
Concentration in ground	= $5 \times 10^{-8}$ ppb
Concentration in the Bottom sediments	= $5 \times 10^{-8}$ ppb

=====

#### 4. Risk Characterization

The toxicological data discussed in the first section indicates that there is a slight hazard associated with the isocyanates. Thus from Table III the LD50 for rats is in the range of 5 - 10 g/kg. In order to place this in proper perspective the LD50 for ethanol is 10 g/kg (Verschueren, 1983). The risk to other animals such as fish, birds etc. appears to be minimal (Brochhagen et al, 1984).

By far the greatest hazard is via inhalation and the sensitization that some workers have experienced (Bayer Chemical, 1991). This has created a situation in the United Kingdom and some States in the USA where "fence line" concentrations in the order of 0.4 ppb of TDI are required (Gilbert, 1988). It will be recalled that this level is very close to the criteria arrived at in section 2 dealing with Dose Response.

Thus the objective is to maintain environmental concentrations at or below 0.4 ppb. As section 3 on Exposure Assessment describes the probability of stack emissions exceeding 0.4 ppb will occur only in the situation where the stack height is short and the exposure occurs in the near vicinity of the stack. Global emissions at the present level of production and any presently planned growth will never cause environmental concentrations to exceed the 0.4 ppb. The reason for this definitive statement is due to the highly reactive nature of the molecules which prevents them from building

up in the environment. Thus the conclusion is reached that the risk from environmental exposure to the isocyanate molecules is insignificant.



#### REFERENCES

Bailey, R., (1991) "Summary of the Chemical and Physical Properties of the Isocyanates" Report prepared for the Int. Isocyanate Institute and given to the Environmental Protection Agency on March 19.

Baughman, G.L., and Lassiter, R.R., (1978) in "Estimating the Hazard of Chemical Substances to Aquatic Life" ed J. Cairns, Jr., ASTM STP 657, Philadelphia, Pa. p 35.

Bayer Chemical Co., (1991) "Basic Reactions of Isocyanates" presented at a Int. Isocyanate Institute workshop in Munich, Germany, January.

Becker, K.H., Bastian, V., and Klein, T., (1988) J. Photochem. and Photobiol. A: Chemistry, 45, 195-205.

Brochhagen, F. K., and Grieveson, B. M., (1984), Cellular Polymers, 3, 11.

C&EN, (1991) "U S Chemical Production Figures for 1990" Chem. and Eng. News, June 24.

Chemical Biotesting Institute, (1991) Draft Report "On the Deterioration of the Octanol Water Partition Coefficients and Water Solubility for TDI and MDI" prepared for the International Isocyanate Institute.

Costle, D., (1980), Fed. Register, 15, p 79318, Nov. 28.

Curtis, M.W., Copeland, T.L., Ward, C.H., (1979), Water Res., 13, 137.

EPA (1986) "Risk Assessment Guidelines of 1986", Office of Emergency and Remedial Response. US Government Printing Office, Washington DC, EPA/540/1-89/002

Frey, H. E., Bujold, A. R., and Sakunma, W. and Y., (1990) Chemical Economics Handbook, published by SRI, Menlo Park, Calif., Sept.

Gilbert, D. S., (1988), J. Cellular Plastics, 24, 178.

Grieveson, B.M., Reeve, B., (1983), Cellular Polymer, 2, 165.

Holdren, M. W., Spicar, C. W., Riggan, R. M., (1984) Am. Ind. Hyg. Assoc. J., 45, 626.

Kirk-Othmer, (1981) "Encyclopedia of Chemical Technology", 3rd Edition, Vol 13.

Kitano, M., Yakabe, Y., and Shimogagawa, Y., (1991) Draft report FE-E-63 PART III prepared for the International Isocyanate Institute.

Loeser, E., (1983), Toxicol. Let., 15, 71, as reported in the Draft Report on the Chemical Hazard Information Profile for TDI by M.L. Daugherty, Oak Ridge National Laboratory, July 1984.

Mackay, D., Paterson, S., Cheung, B., and Neely, W. B., (1985), Chemosphere, 14, 335.

Mackay, D., (1979), Env. Sci. and Technol., 13, 1220.

Morton, M., and Deisz, M. A., (1956) Am. Chem. Soc., September Meeting, Atlantic City, NJ, reported in Farkas and Mills, Ad. in Catalysis 13, 393 (1962).

NAS (1983) "Risk Assessment in the Federal Government: Managing the Process" National Academy of Sciences, Washington, DC.

Neely, W. B., (1985) in "New Approaches in Toxicity Testing and their Application in Human Risk Assessment", ed. by A. P. Li, Raven Press p 235.

Neely, W. B., and Mackay, D., (1982) "Modelling the Fate of Chemicals in the Aquatic Environment" Ann Arbor Press, Ann Arbor, Mich.

Neely, W. B. and Oliver, G. R., (1986) in "Pollutants in a Multi Media Environment" ed Cohen, Y., Plenum Press, New York, NY p 133.

Neely, W.B., (1977), Science of the Total Environ., 8, 267.

NIOSH (1980), "Registry of Toxic Effects of Chemical Substances" ed by Lewis, R.J. and Tatken R. L., published by the US Dept. of Health and Human Services, Nat. Institute for Occupational Safety and Health.

NTP, 1983, National Toxicology Program, Research Triangle Park, NC NIH Publication, # 83-2507.

Schafer, E.W., Booles, W.A., Hurlbut, J., (1983), Arch. Environ. Contam. Toxicol., 12, 355.

Stephanson, M., (1977), Ecotoxicol. Env. Safety, 1, 39.

Turner, B.D., (1970) "Workbook of Atmospheric Dispersion Estimates" National Air Pollution Control Administration, PB-191 482, Cincinnati, Ohio.

Vershueren, K., (1983) "Handbook of Environmental Data on Organic Compounds" 2nd Edition, Van Nostrand, Reinhold Co., New York, NY

Yoshida, K., Shigeoka, T., and Yamauchi, F., (1987), Toxicol. and Environ. Chem., 15, 159.

Yoshida, K., Shigeoka, T., and Yamauchi, F., (1988), Toxicol. and Environ. Chem., 17, 69.

### CERTIFICATE OF AUTHENTICITY

THIS IS TO CERTIFY that the microimages appearing on this microfiche are accurate and complete reproductions of the records of U.S. Environmental Protection Agency documents as delivered in the regular course of business for microfilming.

Data produced 1 28 94 Marcia Tubelino  
(Month) (Day) (Year) Camera Operator

Place Syracuse New York  
(City) (State)

